

# **CATALYZED HYDROGEN DESORPTION IN MG-BASED HYDROGEN STORAGE MATERIAL AND METHODS FOR PRODUCTION THEREOF**

## **FILED OF THE INVENTION**

The instant invention relates generally to hydrogen storage materials and more specifically magnesium-based hydrogen storage materials in which hydrogen desorption is catalyzed by materials which are insoluble in said magnesium-based hydrogen storage material. The insoluble catalytic material may be in the form of: 1) discrete dispersed regions of catalytic material in a hydrogen storage material bulk; 2) discrete dispersed regions on the surface of particles of the hydrogen storage material; 3) a continuous or semi-continuous layer of catalytic material on the surface of bulk or particulate hydrogen storage material; or 4) combinations thereof.

## **BACKGROUND OF THE INVENTION**

Growing energy needs have prompted specialists to take cognizance of the fact that the traditional energy resources, such as coal, petroleum or natural gas, are not inexhaustible, or at least that they are becoming costlier all the time, and that it is advisable to consider replacing them with hydrogen.

Hydrogen may be used, for example, as fuel for internal-combustion engines in place of hydrocarbons. In this case it has the advantage of eliminating atmospheric pollution through the formation of oxides of carbon, nitrogen and sulfur upon combustion of the hydrocarbons. Hydrogen may also be used to fuel hydrogen-air fuel cells for production of the electricity needed for electric motors.

One of the problems posed by the use of hydrogen is its storage and transportation. A number of solutions have been proposed:

Hydrogen may be stored under high pressure in steel cylinders, but this approach has the drawback of requiring hazardous and heavy containers which are difficult to handle (in addition to having a low storage capacity of about 1% by weight). Hydrogen may also be stored in cryogenic containers, but this entails the disadvantages associated with the use of cryogenic liquids; such as, for example, the high cost of the containers, which also require careful handling. There are also "boil off" losses of about 2-5% per day.

Another method of storing hydrogen is to store it in the form of a hydride, which then is decomposed at the proper time to furnish hydrogen. The hydrides of iron-titanium, lanthanum-nickel, vanadium, and magnesium have been used in this manner, as described in French Pat. No. 1,529,371.

Since the initial discovery that hydrogen could be stored in a safe, compact solid state metal hydride form, researchers have been trying to produce hydrogens storage materials which have optimal properties. Generally, the ideal material properties that these researchers have been attempting to achieve are: 1) a high hydrogen storage capacity; 2) light weight materials; 3)adequate hydrogen absorption/desorption temperatures; 4) adequate absorption/desorption pressures; 5) fast absorption kinetics; and 6) a long absorption/desorption cycle life. In addition to these material properties, ideal materials would be inexpensive and easy to produce.

The  $\text{MgH}_2$ --Mg system is the most appropriate of all known metal-hydride and metal systems that can be used as reversible hydrogen-storage systems because it has the highest percentage by weight (7.65% by weight) of theoretical capacity for hydrogen storage and hence the highest

theoretical energy density (2332 Wh/kg; Reilly & Sandrock, Spektrum der Wissenschaft, Apr. 1980, 53) per unit weight of storage material.

Although this property and the relatively low price of magnesium make the  $\text{MgH}_2$  --Mg seem the optimum hydrogen storage system for transportation, for hydrogen-powered vehicles that is, its unsatisfactory kinetics have prevented it from being used up to the present time. It is known for instance that pure magnesium can be hydrided only under drastic conditions at temperatures of perhaps 400 °C, and then only very slowly and incompletely. The dehydriding rate of the resulting hydride is also unacceptable for a hydrogen storage material (Genossar & Rudman, Z. f. Phys. Chem., Neue Folge 116, 215 [1979], and the literature cited therein).

Moreover, the hydrogen storage capacity of a magnesium reserve diminishes during the charging/discharging cycles. This phenomenon may be explained by a progressive poisoning of the surface, which during charging renders the magnesium atoms located in the interior of the reserve inaccessible to the hydrogen.

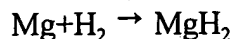
To expel the hydrogen in conventional magnesium or magnesium/nickel reserve systems, temperatures of more than 250 °C are required, with a large supply of energy at the same time. The high temperature level and the high energy requirement for expelling the hydrogen have the effect that, for example, a motor vehicle with an internal combustion engine, cannot exclusively be operated from these alloys. This occurs because the energy contained in the exhaust gas, in the most favorable case (full load), is sufficient for meeting only 50% of the hydrogen requirement of the internal combustion engine from a magnesium or magnesium/nickel alloy. Thus, the remaining hydrogen demand must be taken from another hydride alloy. For example, this alloy can be titanium/iron hydride (a typical low-temperature hydride store) which can be operated at

temperatures down to below 0 °C. These low-temperature hydride alloys have the disadvantage of having a low hydrogen storage capacity.

Storage materials have been developed in the past, which have a relatively high storage capacity but from which hydrogen is nevertheless expelled at temperatures of up to about 250 °C. U.S. Pat. No. 4,160,014 describes a hydrogen storage material of the formula  $Ti_{[1-x]}Zr_{[x]}Mn_{[2-y-z]}Cr_{[y]}V_{[z]}$ , wherein  $x=0.05$  to  $0.4$ ,  $y=0$  to  $1$  and  $z=0$  to  $0.4$ . Up to about 2% by weight of hydrogen can be stored in such an alloy. In addition to this relatively low storage capacity, these alloys also have the disadvantage that the price of the alloy is very high when metallic vanadium is used.

Moreover, U.S. Pat. No. 4,111,689 has disclosed a storage alloy which comprises 31 to 46% by weight of titanium, 5 to 33% by weight of vanadium and 36 to 53% by weight of iron and/or manganese. Although alloys of this type have a greater storage capacity for hydrogen than the alloy according to U.S. Pat. No. 4,160,014, hereby incorporated by reference, they have the disadvantage that temperatures of at least 250 °C. are necessary in order to completely expel the hydrogen. At temperatures of up to about 100 °C., about 80% of the hydrogen content can be discharged in the best case. However, a high discharge capacity, particularly at low temperatures, is frequently necessary in industry because the heat required for liberating the hydrogen from the hydride stores is often available only at a low temperature level.

In contrast to other metals or metal alloys, especially such metal alloys which contain titanium or lanthanum, magnesium is preferred for the storage of hydrogen not only because of its lower material costs, but above all, because of its lower specific weight as a storage material. However, the hydriding



is, in general, more difficult to achieve with magnesium, inasmuch as the surface of the magnesium will rapidly oxidize in air so as to form stable  $\text{MgO}$  and/or  $\text{Mg}(\text{OH})_2$  surface layers. These layers inhibit the dissociation of hydrogen molecules, as well as the absorption of produced hydrogen atoms and their diffusion from the surface of the granulate particles into the magnesium storage mass.

Intensive efforts have been devoted in recent years to improve the hydriding ability of magnesium by doping or alloying it with such individual foreign metals as aluminum (Douglass, *Metall. Trans.* 6a, 2179 [1975]) indium (Mintz, Gavra, & Hadari, *J. Inorg. Nucl. Chem.* 40, 765 [1978]), or iron (Welter & Rudman, *Scripta Metallurgica* 16, 285 [1982]), with various foreign metals (German Offenlegungsschriften 2 846 672 and 2 846 673), or with intermetallic compounds like  $\text{Mg}_2\text{Ni}$  or  $\text{Mg}_2\text{Cu}$  (Wiswall, *Top Appl. Phys.* 29, 201 [1978] and Genossar & Rudman, *op. cit.*) and  $\text{LaNi}_5$  (Tanguy et al., *Mater. Res. Bull.* 11, 1441 [1976]).

Although these attempts did improve the kinetics somewhat, certain essential disadvantages have not yet been eliminated from the resulting systems. The preliminary hydriding of magnesium doped with a foreign metal or intermetallic compound still demands drastic reaction conditions, and the system kinetics will be satisfactory and the reversible hydrogen content high only after many cycles of hydriding and dehydriding. Considerable percentages of foreign metal or of expensive intermetallic compound are also necessary to improve kinetic properties. Furthermore, the storage capacity of such systems are generally far below what would theoretically be expected for  $\text{MgH}_2$ .

It is known that the storage quality of magnesium and magnesium alloys can also be enhanced by the addition of materials which may help to break up stable oxides of magnesium. For

example, such an alloy is  $\text{Mg}_2\text{Ni}$ , in which the Ni appears to form unstable oxides. In this alloy, thermodynamic examinations indicated that the surface reaction  $\text{Mg}_2\text{Ni} + \text{O}_2 \rightarrow 2\text{MgO} + \text{Ni}$  extended over nickel metal inclusions which catalyze the hydrogen dissociation-absorption reaction. Reference may be had to A. Seiler et al., *Journal of Less-Common Metals* 73, 1980, pages 193 et seq.

One possibility for the catalysis of the hydrogen dissociation-absorption reaction on the surface of magnesium lies also in the formation of a two-phase alloy, wherein the one phase is a hydride former, and the other phase is a catalyst. Thus, it is known to employ galvanically-nickel plated magnesium as a hydrogen storage, referring to F. G. Eisenberg et al. *Journal of Less-Common Metals* 74, 1980, pages 323 et seq. However, there were encountered problems during the adhesion and the distribution of the nickel over the magnesium surface.

In order to obtain an extremely dense and good adherent catalyst phase under the formation alone of equilibrium phases, it is also known that for the storage of hydrogen there can be employed an eutectic mixture of magnesium as a hydride-forming phase in conjunction with magnesium copper ( $\text{Mg}_2\text{Cu}$ ), referring to J. Genossar et al., *Zeitschrift für Physikalische Chemie Neue Folge* 116, 1979, pages 215 et seq. The storage capacity per volume of material which is achieved through this magnesium-containing granulate does not, however, meet any high demands because of the quantity of magnesium copper which is required for the eutectic mixture.

The scientists of this era looked at various materials and postulated that a particular crystalline structure is required for hydrogen storage, see, for example, "Hydrogen Storage in Metal Hydride", *Scientific American*, Vol. 242, No. 2, pp. 118-129, February, 1980. It was found that it

is possible to overcome many of the disadvantages of the prior art materials by utilizing a different class of materials, disordered hydrogen storage materials. For example, U.S. Pat. No. 4,265,720 to Guenter Winstel for "Storage Materials for Hydrogen" describes a hydrogen storage body of amorphous or finely crystalline silicon. The silicon is preferably a thin film in combination with a suitable catalyst and on a substrate.

Laid-open Japanese Patent Application No. 55-167401, "Hydrogen Storage Material," in the name of Matsumoto et al, discloses bi or tri-element hydrogen storage materials of at least 50 volume percent amorphous structure. The first element is chosen from the group Ca, Mg, Ti, Zr, Hf, V, Nb, Ta, Y and lanthanides, and the second from the group Al, Cr, Fe, Co, Ni, Cu, Mn and Si. A third element from the group B, C, P and Ge can optionally be present. According to the teaching of No. 55-167401, the amorphous structure is needed to overcome the problem of the unfavorably high desorption temperature characteristic of most crystalline systems. A high desorption temperature (above, for example, 150 °C.) severely limits the uses to which the system may be put.

According to Matsumoto et al, the material of at least 50% amorphous structure will be able to desorb at least some hydrogen at relatively low temperatures because the bonding energies of the individual atoms are not uniform, as is the case with crystalline material, but are distributed over a wide range.

Matsumoto et al claims a material of at least 50% amorphous structure. While Matsumoto et al does not provide any further teaching about the meaning of the term "amorphous," the scientifically accepted definition of the term encompasses a maximum short range order of about 20 Angstroms or less.

The use by Matsumoto et al of amorphous structure materials to achieve better desorption kinetics due to the non-flat hysteresis curve is an inadequate and partial solution. The other problems found in crystalline hydrogen storage materials, particularly low useful hydrogen storage capacity at moderate temperature, remain.

However, even better hydrogen storage results, i.e., long cycle life, good physical strength, low absorption/desorption temperatures and pressures, reversibility, and resistance to chemical poisoning, may be realized if full advantage is taken of modification of disordered metastable hydrogen storage materials. Modification of disordered structurally metastable hydrogen storage materials is described in U.S. Pat. No. 4,431,561 to Stanford R. Ovshinsky et al. for "Hydrogen Storage Materials and Method of Making the Same". As described therein, disordered hydrogen storage materials, characterized by a chemically modified, thermodynamically metastable structure, can be tailor-made to possess all the hydrogen storage characteristics desirable for a wide range of commercial applications. The modified hydrogen storage material can be made to have greater hydrogen storage capacity than do the single phase crystalline host materials. The bonding strengths between the hydrogen and the storage sites in these modified materials can be tailored to provide a spectrum of bonding possibilities thereby to obtain desired absorption and desorption characteristics. Disordered hydrogen storage materials having a chemically modified, thermodynamically metastable structure also have a greatly increased density of catalytically active sites for improved hydrogen storage kinetics and increased resistance to poisoning.

The synergistic combination of selected modifiers incorporated in a selected host matrix provides a degree and quality of structural and chemical modification that stabilizes chemical, physical, and electronic structures and conformations amenable to hydrogen storage.



The framework for the modified hydrogen storage materials is a lightweight host matrix. The host matrix is structurally modified with selected modifier elements to provide a disordered material with local chemical environments which result in the required hydrogen storage properties.

Another advantage of the host matrix described by Ovshinsky, et al. is that it can be modified in a substantially continuous range of varying percentages of modifier elements. This ability allows the host matrix to be manipulated by modifiers to tailor-make or engineer hydrogen storage materials with characteristics suitable for particular applications. This is in contrast to multi-component single phase host crystalline materials which generally have a very limited range of stoichiometry available. A continuous range of control of chemical and structural modification of the thermodynamics and kinetics of such crystalline materials therefore is not possible.

A still further advantage of these disordered hydrogen storage materials is that they are much more resistant to poisoning. As stated before, these materials have a much greater density of catalytically active sites. Thus, a certain number of such sites can be sacrificed to the effects of poisonous species, while the large number of non-poisoned active sites still remain to continue to provide the desired hydrogen storage kinetics.

Another advantage of these disordered materials is that they can be designed to be mechanically more flexible than single phase crystalline materials. The disordered materials are thus capable of more distortion during expansion and contraction allowing for greater mechanical stability during the absorption and desorption cycles.

One drawback to these disordered materials is that, in the past, some of the Mg based alloys have been difficult to produce. Particularly those materials that did not form solutions in the melt. Also, the most promising materials (i.e. magnesium based materials) were extremely difficult to

make in bulk form. That is, while thin-film sputtering techniques could make small quantities of these disordered alloys, there was no bulk preparation technique.

Then in the mid 1980's, two groups developed mechanical alloying techniques to produce bulk disordered magnesium alloy hydrogen storage materials. Mechanical alloying was found to facilitate the alloying of elements with vastly different vapor pressures and melting points (such as Mg with Fe or Ti etc.), especially when no stable intermetallic phases exist. Conventional techniques like induction melting have been found to be inadequate for such purposes.

The first of the two groups was a team of French scientists which investigated mechanical alloying of materials of the Mg-Ni system and their hydrogen storage properties. See Senegas, et al., "Phase Characterization and Hydrogen Diffusion Study in the Mg-Ni-H System", *Journal of the Less-Common Metals*, Vol. 129, 1987, pp. 317-326 (binary mechanical alloys of Mg and Ni incorporating 0, 10, 25 and 55 wt. % Ni); and also, Song, et al. "Hydriding and Dehydriding Characteristics of Mechanically Alloyed Mixtures Mg - x wt. % Ni (x=5, 10, 25 and 55)", *Journal of the Less-Common Metals*, Vol. 131, 1987, pp. 71-79 (binary mechanical alloys of Mg and Ni incorporating 5, 10, 25 and 55 wt. % Ni).

The second of the two groups was a team of Russian scientists which investigated the hydrogen storage properties of binary mechanical alloys of magnesium and other metals. See Ivanov, et al., "Mechanical Alloys of Magnesium--New Materials For Hydrogen Energy", *Doklady Physical Chemistry (English Translation)* vol. 286:1-3, 1986, pp. 55-57, (binary mechanical alloys of Mg with Ni, Ce, Nb, Ti, Fe, Co, Si and C); also, Ivanov, et al. "Magnesium Mechanical Alloys for Hydrogen Storage", *Journal of the Less-Common Metals*, vol. 131, 1987, pp. 25-29 (binary mechanical alloys of Mg with Ni, Fe, Co, Nb and Ti); and Stepanov, et al., "Hydriding Properties

of Mechanical Alloys of Mg-Ni", Journal of the Less-Common Metals, vol. 131, 1987, pp. 89-97 (binary mechanical alloys of the Mg-Ni system). See also the collaborative work between the French and Russian groups, Konstanchuk, et al., "The Hydriding Properties of a Mechanical Alloy With Composition Mg-25% Fe", Journal of the Less-Common Metals, vol. 131, 1987, pp. 181-189 (binary mechanical alloy of Mg and 25 wt. % Fe).

Later, in the late 1980's and early 1990's, a Bulgarian group of scientists (sometimes in collaboration with the Russian group of scientists) investigated the hydrogen storage properties of mechanical alloys of magnesium and metal oxides. See Khrussanova, et al., "Hydriding Kinetics of Mixtures Containing Some 3d-Transition Metal Oxides and Magnesium", Zeitschrift fur Physikalische Chemie Neue Folge, Munchen, vol. 164, 1989, pp. 1261-1266 (comparing binary mixtures and mechanical alloys of Mg with  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$ ); and Peshev, et al., "Surface Composition of Mg-- $\text{TiO}_2$  Mixtures for Hydrogen Storage, Prepared by Different Methods", Materials Research Bulletin, vol. 24, 1989, pp. 207-212 (comparing conventional mixtures and mechanical alloys of Mg and  $\text{TiO}_2$ ). See also, Khrussanova, et al., "On the Hydriding of a Mechanically Alloyed Mg(90%)-- $\text{V}_2\text{O}_5$  (10%) Mixture", International Journal of Hydrogen Energy, vol. 15, No. 11, 1990, pp. 799-805 (investigating the hydrogen storage properties of a binary mechanical alloy of Mg and  $\text{V}_2\text{O}_5$ ); and Khrussanova, et al., "Hydriding of Mechanically Alloyed Mixtures of Magnesium With  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and NiO", Materials Research Bulletin, vol. 26, 1991, pp. 561-567 (investigating the hydrogen storage properties of a binary mechanical alloys of Mg with and  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and NiO). Finally, see also, Khrussanova, et al., "The Effect of the d-Electron Concentration on the Absorption Capacity of Some Systems for Hydrogen Storage", Materials Research Bulletin, vol. 26, 1991, pp. 1291-1298 (investigating d-electron concentration effects on

the hydrogen storage properties of materials, including mechanical alloys of Mg and 3-d metal oxides); and Mitov, et al., "A Mossbauer Study of a Hydrided Mechanically Alloyed Mixture of Magnesium and Iron(III) Oxide", Materials Research Bulletin, vol. 27, 1992, pp. 905-910 (Investigating the hydrogen storage properties of a binary mechanical alloy of Mg and  $\text{Fe}_2\text{O}_3$ ).

More recently, a group of Chinese scientists have investigated the hydrogen storage properties of some mechanical alloys of Mg with other metals. See, Yang, et al., "The Thermal Stability of Amorphous Hydride  $\text{Mg}_{50}\text{Ni}_{50}\text{H}_{54}$  and  $\text{Mg}_{30}\text{Ni}_{70}\text{H}_{45}$ ", Zeitschrift fur Physikalische Chemie, Munchen, vol. 183, 1994, pp. 141-147 (Investigating the hydrogen storage properties of the mechanical alloys  $\text{Mg}_{50}\text{Ni}_{50}$  and  $\text{Mg}_{30}\text{Ni}_{70}$ ); and Lei, et al., "Electrochemical Behavior of Some Mechanically Alloyed Mg-Ni-based Amorphous Hydrogen Storage Alloys", Zeitschrift fur Physikalische Chemie, Munchen, vol. 183, 1994, pp. 379-384 (investigating the electrochemical [i.e. Ni-MH battery] properties of some mechanical alloys of Mg--Ni with Co, Si, Al, and Co-Si).

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Short-range, or local, order is elaborated on in U.S. Pat. No. 4,520,039 to Ovshinsky, entitled Compositionally Varied Materials and Method for Synthesizing the Materials, the contents of which are incorporated by reference. This patent disclosed that disordered materials do not require any periodic local order and how spatial and orientational placement of similar or dissimilar atoms or groups of atoms is possible with such increased precision and control of the local configurations that it is possible to produce qualitatively new phenomena. In addition, this patent discusses that the atoms used need not be restricted to "d band" or "f band" atoms, but can be any atom in which the controlled aspects of the interaction with the local environment and/or orbital overlap plays a significant role physically, electronically, or chemically so as to affect physical properties and hence the functions of the materials. The elements of these materials offer a variety of bonding possibilities due to the multidirectionality of d-orbitals. The multidirectionality ("porcupine effect") of d-orbitals provides for a tremendous increase in density and hence active storage sites. These techniques result

in means of synthesizing new materials which are disordered in several different senses simultaneously.

Ovshinsky had previously shown that the number of surface sites could be significantly increased by making an amorphous film in which the bulk thereof resembled the surface of the desired relatively pure materials. Ovshinsky also utilized multiple elements to provide additional bonding and local environmental order which allowed the material to attain the required electrochemical characteristics. As Ovshinsky explained in Principles and Applications of Amorphicity, Structural Change, and Optical Information Encoding, 42 Journal De Physique at C4-1096 (October 1981):

Amorphicity is a generic term referring to lack of X-ray diffraction evidence of long-range periodicity and is not a sufficient description of a material. To understand amorphous materials, there are several important factors to be considered: the type of chemical bonding, the number of bonds generated by the local order, that is its coordination, and the influence of the entire local environment, both chemical and geometrical, upon the resulting varied configurations. Amorphicity is not determined by random packing of atoms viewed as hard spheres nor is the amorphous solid merely a host with atoms imbedded at random. Amorphous materials should be viewed as being composed of an interactive matrix whose electronic configurations are generated by free energy forces and they can be specifically defined by the chemical nature and coordination of the constituent atoms. Utilizing multi-orbital elements and various preparation techniques, one can outwit the normal relaxations that reflect equilibrium conditions and, due to the three-dimensional freedom of the amorphous state, make entirely new types of amorphous materials--chemically modified materials . . .

Once amorphicity was understood as a means of introducing surface sites in a film, it was possible to produce "disorder" that takes into account the entire spectrum of effects such as porosity, topology, crystallites, characteristics of sites, and distances between sites. Thus, rather than searching for material changes that would yield ordered materials having a maximum number of accidentally occurring surface bonding and surface irregularities, Ovshinsky and his team at ECD began constructing "disordered" materials where the desired irregularities were tailor made. See, U.S. Pat. No. 4,623,597, the disclosure of which is incorporated by reference.

The term "disordered", as used herein to refer to electrochemical electrode materials, corresponds to the meaning of the term as used in the literature, such as the following:

A disordered semiconductor can exist in several structural states. This structural factor constitutes a new variable with which the physical properties of the [material] . . . can be controlled. Furthermore, structural disorder opens up the possibility to prepare in a metastable state new compositions and mixtures that far exceed the limits of thermodynamic equilibrium. Hence, we note the following as a further distinguishing feature. In many disordered [materials] . . . it is possible to control the short-range order parameter and thereby achieve drastic changes in the physical properties of these materials, including forcing new coordination numbers for elements . . .

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S. R. Ovshinsky, The Shape of Disorder, 32 Journal of Non-Crystalline Solids at 22 (1979) (emphasis added).

The "short-range order" of these disordered materials are further explained by Ovshinsky in The Chemical Basis of Amorphicity: Structure and Function, 26:8-9 Rev. Roum. Phys. at 893-903 (1981):

[S]hort-range order is not conserved . . . Indeed, when crystalline symmetry is destroyed, it becomes impossible to retain the same short-range order. The reason for

this is that the short-range order is controlled by the force fields of the electron orbitals therefore the environment must be fundamentally different in corresponding crystalline and amorphous solids. In other words, it is the interaction of the local chemical bonds with their surrounding environment which determines the electrical, chemical, and physical properties of the material, and these can never be the same in amorphous materials as they are in crystalline materials . . . The orbital relationships that can exist in three-dimensional space in amorphous but not crystalline materials are the basis for new geometries, many of which are inherently anti-crystalline in nature. Distortion of bonds and displacement of atoms can be an adequate reason to cause amorphicity in single component materials. But to sufficiently understand the amorphicity, one must understand the three-dimensional relationships inherent in the amorphous state, for it is they which generate internal topology incompatible with the translational symmetry of the crystalline lattice . . . What is important in the amorphous state is the fact that one can make an infinity of materials that do not have any crystalline counterparts, and that even the ones that do are similar primarily in chemical composition. The spatial and energetic relationships of these atoms can be entirely different in the amorphous and crystalline forms, even though their chemical elements can be the same . . .

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Based on these principles of disordered materials, described above, three families of extremely efficient electrochemical hydrogen storage negative electrode materials were formulated. These families of negative electrode materials, individually and collectively, will be referred to hereinafter as "Ovonic." One of the families is the La-Ni<sub>5</sub> -type negative electrode materials which have recently been heavily modified through the addition of rare earth elements such as Ce, Pr, and Nd and other metals such as Mn, Al, and Co to become disordered multicomponent alloys, i.e., "Ovonic". The second of these families is the Ti-Ni-type negative electrode materials which were introduced and developed by the assignee of the subject invention and have been heavily modified

through the addition of transition metals such as Zr and V and other metallic modifier elements such as Mn, Cr, Al, Fe, etc. to be disordered, multicomponent alloys, i.e., "Ovonic." The third of these families are the disordered, multicomponent MgNi-type negative electrode materials described in U.S. Patent Nos.: 5,506,069; 5,616,432; and 5,554,456 (the disclosures of which are hereby incorporated by reference).

Based on the principles expressed in Ovshinsky's '597 Patent, the Ovonic Ti-V-Zr-Ni type active materials are disclosed in U.S. Pat. No. 4,551,400 to Sapru, Fetcenko, et al. ("the '400 Patent"), the disclosure of which is incorporated by reference. This second family of Ovonic materials reversibly form hydrides in order to store hydrogen. All the materials used in the '400 Patent utilize a Ti-V-Ni composition, where at least Ti, V, and Ni are present with at least one or more of Cr, Zr, and Al. The materials of the '400 Patent are generally multiphase polycrystalline materials, which may contain, but are not limited to, one or more phases of Ti-V-Zr-Ni material with C.sub.14 and C.sub.15 type crystal structures. Other Ovonic Ti-V-Zr-Ni alloys are described in commonly assigned U.S. Pat. No. 4,728,586 ("the '586 Patent"), titled Enhanced Charge Retention Electrochemical Hydrogen Storage Alloys and an Enhanced Charge Retention Electrochemical Cell, the disclosure of which is incorporated by reference.

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The characteristic surface roughness of the metal electrolyte interface is a result of the disordered nature of the material as disclosed in commonly assigned U.S. Pat. No. 4,716,088 to Reichman, Venkatesan, Fetcenko, Jeffries, Stahl, and Bennet, the disclosure of which is incorporated by reference. Since all of the constituent elements, as well as many alloys and phases thereof, are present throughout the metal, they are also represented at the surfaces and at cracks which form in the metal/electrolyte interface. Thus, the characteristic surface roughness is descriptive of the interaction of the physical and chemical properties of the host metals as well as of the alloys and crystallographic phases of the alloys, in an alkaline environment. The microscopic chemical,



physical, and crystallographic parameters of the individual phases within the hydrogen storage alloy material are important in determining its macroscopic electrochemical characteristics.

In addition to the physical nature of its roughened surface, it has been observed that V-Ti-Zr-Ni type alloys tend to reach a steady state surface condition and particle size. This steady state surface condition is characterized by a relatively high concentration of metallic nickel. These observations are consistent with a relatively high rate of removal through precipitation of the oxides of titanium and zirconium from the surface and a much lower rate of nickel solubilization. The resultant surface has a higher concentration of nickel than would be expected from the bulk composition of the negative hydrogen storage electrode. Nickel in the metallic state is electrically conductive and catalytic, imparting these properties to the surface. As a result, the surface of the negative hydrogen storage electrode is more catalytic and conductive than if the surface contained a higher concentration of insulating oxides.

The surface of the negative electrode, which has a conductive and catalytic component--the metallic nickel--interacts with metal hydride alloys in catalyzing the electrochemical charge and discharge reaction steps, as well as promoting fast gas recombination.

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Finally, in U.S. Patent No. 5,616,432 ('432 patent) inventors of Ovonic Battery Company produced Mg-Ni-Co-Mn alloys similar to the base alloys of the present inventive composite hydrogen storage material. The storage capacity of these alloys was limited to about 2.7 weight percent and none of the stored hydrogen was desorbed from the alloy at 30 °C. Figure 1 plots the PCT curve of the '432 patents thin film alloy (reference symbol  $\Delta$ ) with that of the present composite hydrogen storage material (reference symbol  $\blacklozenge$ ). As can be seen, the hydrogen storage composite materials of the present invention adsorb more than 4 weight percent of hydrogen, and what is even more remarkable is that this hydrogen can be desorbed at a temperature of 30 °C.

The present invention uses catalysis to promote hydrogen adsorption/desorption in a relatively pure Mg material using insoluble catalytic material and reduces the desorption temperature of the high capacity Mg-based materials by adding some grain grow inhibitors.

## SUMMARY OF THE INVENTION

The instant invention provides for a magnesium-based hydrogen storage material including magnesium or a magnesium-based hydrogen storage alloy; and a hydrogen desorption catalyst which is insoluble in said magnesium-based hydrogen storage alloy and is in the form of: 1) discrete dispersed regions of catalytic material within the bulk of said magnesium or magnesium-based hydrogen storage alloy; 2) discrete dispersed regions on the surface of particles of said magnesium or magnesium-based hydrogen storage alloy; 3) a continuous or semi-continuous layer of catalytic material on the surface of said magnesium or magnesium-based hydrogen storage alloy which is in bulk or particulate form; or 4) combinations thereof. Preferably the magnesium-based hydrogen storage alloy includes at least 80 atomic percent magnesium and may include aluminum. Preferably the hydrogen desorption catalyst includes iron and may further include one or more elements selected from the group consisting of B, Cu, Pd, V, Ni, C, Mn, Zr, Rb, Nb, Ti, U and Sc.

The instant invention further includes methods of making the magnesium-based hydrogen storage material. One such method includes a) mixing powders of the magnesium or magnesium-based hydrogen storage alloy and powders of the hydrogen desorption catalyst; b) pressing the mixed powders into a compact; and c) sintering/annealing said compact at a temperature between 450 °C and 600 °C. Preferably the sintering/annealing is performed for at least 10 hours.

Another such method includes a) forming a melt of powders of the magnesium or magnesium-based hydrogen storage alloy and powders of the hydrogen desorption catalyst in a protective atmosphere; b) stirring the melt to insure suspension of the insoluble powders of the hydrogen desorption catalyst within the molten magnesium or magnesium-based hydrogen storage

alloy; and c) rapidly quenching the stirred melt such that the suspended insoluble powders of the hydrogen desorption catalyst are well distributed in the solidified magnesium or magnesium-based hydrogen storage alloy.

Yet another method includes; a) mixing powders of said magnesium or magnesium-based hydrogen storage alloy and powders of said hydrogen desorption catalyst; and b) mechanically alloying the mixture in an attritor such that powder particles of said hydrogen desorption catalyst are embedded in at least the surface of powder particles of said magnesium or magnesium-based hydrogen storage alloy. Preferably heptane and carbon powder are used as grinding aids during mechanical alloying of said mixture.

A further method includes; a) providing bulk or particulate magnesium or magnesium-based hydrogen storage alloy; and b) depositing a continuous or semi-continuous layer of catalytic material onto the surface of said bulk or particulate magnesium or magnesium-based hydrogen storage alloy by vapor deposition, electrolytic coating or electroless coating. Preferably the coating is formed by evaporation of said catalytic material and is about 100 angstroms thick.

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The catalyst may be distributed in multiple ways by combining the above techniques. The bulk or particulate magnesium or magnesium-based hydrogen storage alloy may be produced by; a) forming a melt of said magnesium or magnesium-based hydrogen storage alloy; and b) rapidly quenching said magnesium or magnesium-based hydrogen storage alloy by a bulk quick quenching method. Useful bulk quick quenching method includes melt spinning, centrifugal atomization, gas atomization, or water atomization.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a scanning electron micrograph (SEM) taken in back-scattering mode of a hydrogen storage material of the instant invention made from pure metal powders pressed and sintered at a temperature above 500° C for 22 hours under vacuum;

Figure 2 is an X-ray diffraction pattern of the material of figure 1;

Figure 3 is a plot of the pressure-concentration-isotherm (PCT) curve for the material of figure 1 measured at 240 °C;

Figure 4 plots the percent hydrogen absorption versus time (i.e. absorption rates) of the material of figure 1 at various temperatures;

Figure 5 plots the percent of hydrogen desorbed versus time (i.e. desorption rate) of the material of figure 1 at 240 °C;

Figure 6 plots the PCT curves of samples having the same composition as that of figure 1, but sintered/annealed at 570 and 600 °C respectively;

Figure 7 is an SEM back-scattering micrograph of another material according to the instant invention having the same composition as the material of figure 1 but formed by mechanical alloying;

Figure 8 is the XRD plot of the material of figure 7;

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Figure 9 is a plot of the PCT curve of the material of figure 7, measured at 240 °C;

Figure 10 plots the PCT absorption curves of the material of figure 7 at 240 °C, 210 °C, 180 °C, and 150 °C;

Figure 11 is an SEM backscattered photomicrograph of a cross-section of a melt spun ribbon of a very uniform Mg-Al alloy used to produce a material according to the instant invention;

Figure 12 shows a PCT plot of a hydrogen storage material according to the instant invention at 150 °C, the material was produced using the material of figure 11 which is mechanically alloyed, pressed flat onto an expanded nickel substrate and coated on both sides with 100 angstroms of iron;

Figure 13 is a comparison plot of the maximum reversible hydrogen storage capacities at various temperatures for the materials of figures 1, 7 and 12;

Figure 14 is an SEM micrograph of a cross-section of an ingot produced by induction melting and casting the elemental metal powders required to produce the composition of the material of figure 1, while continuously stirring the melt to suspend insoluble materials;

Figure 15 is a schematic depiction of the microstructure of the hydrogen storage powder materials produced by various processing methods of the instant invention.

### DETAILED DESCRIPTION OF THE INVENTION

The present inventors have found that iron and/or other elements which have a very low solubility in Mg, to a Mg based alloy prohibits the grain growth of Mg or Mg-based crystallites within the alloy and catalyze the desorption of hydrogen from such Mg material. Thus, the instant invention provides for magnesium-based hydrogen storage materials in which hydrogen desorption is catalyzed by iron and/or other elements which are substantially insoluble in said magnesium-based hydrogen storage material. The insoluble catalytic material may be in the form of: 1) discrete dispersed regions of catalytic material in a hydrogen storage material bulk; 2) discrete dispersed regions on the surface of particles of the hydrogen storage material; 3) a continuous or semi-continuous layer of catalytic material on the surface of bulk or particulate hydrogen storage material; or 4) combinations thereof. The catalytic material can be added during the alloying process by special rapid quenching methods; or by mechanical alloying methods. The catalytic material can also be applied to the surface of the magnesium-based alloy by processes such as thermal evaporation, magnetic sputtering, or by electrolytic or electroless plating methods.

Elements which have almost no solid solubility in Mg may be used as grain grow inhibitors/desorption catalysts. Specific candidates include Fe (with a solubility of 0.00043 at. %), Rb (with a solubility of <0.05 at.%), Nb, Ti, V, and U. Additionally, elements having limited solid solubility in magnesium may be used as part of an intermetallic compound with the elements listed

above to form a grain boundary crystallite growth inhibiting material. Candidates include Mn (solubility = 0.99 at. % in Mg) and Zr (solubility = 1.042 at. % in Mg).

### Example 1

Raw materials consisting of pure metal powders of magnesium (99.8%, -325 mesh), aluminum (99.5%, -325 mesh), iron (99.9+%, 10 micron) and other minor constituents were mixed in an agate mortar-pestle. Ten different compositions were produced, and their compositions in weight percent are listed in Table 1. A hardened steel die was used to press the mixed powders into a pellet of 1 cm diameter and 1 cm long. The pressed pellet was placed in a quartz tube and was sintered at a temperature above 500° C for 22 hours under vacuum.

Table I. Chemical composition (all numbers are in weight percentage)

Alloy Number	Mg	Al	Fe	B	Cu	Pd	V	Ni	C	Sc
MM-1	88.8	2.7	8.5	-	-	-	-	-	-	-
MM-2	87	3	9	1	-	-	-	-	-	-
MM-3	86	3	9	2	-	-	-	-	-	-
MM-4	86	3	9	-	2	-	-	-	-	-
MM-5	87	3	6	-	4	-	-	-	-	-
MM-6	87	3	8	-	-	2	-	-	-	-
MM-7	87	3	8	-	-	-	2	-	-	-
MM-8	87	-	9	-	-	-	-	4	-	-
MM-9	87	-	9	-	-	-	-	-	4	-
MM-10	87	3	7	-	-	-	-	-	-	3

Figure 1 is a scanning electron micrograph (SEM) taken in back-scattering mode of an MM-1 sample sintered/annealed at 500°C. The SEM indicates phase segregation of Fe and an  $Al_3Fe_2$  intermetallic compounds imbedded in the main Mg matrix. The Fe and Fe-rich phases are about a few microns in diameter and the proximity is about 10-20 microns. Figure 2 is an X-ray diffraction pattern of the sample, which was recorded on a Rigaku Mini Flex. It clearly indicates the co-existence of Fe and FeAl with the main Mg phase.

Figure 3 is a plot of the pressure-concentration-isotherm (PCT) curve for the same material measured at 240 °C. As can be seen, a very flat plateau pressure was found at around 1800 Torr. The entire absorption/desorption is reversible with a maximum capacity at 5 wt.% of hydrogen. Figure 4 plots the percent hydrogen absorption versus time (i.e. absorption rates) for the MM-1 alloy material at various temperatures. As indicated in Figure 4, as the temperature increases, the absorption kinetics improves. As can also be seen, if the absorption temperature is too high, the maximum storage capacity will be reduced (see example at 270 °C). Thus it seems that finding an optimized absorption temperature is a balance between kinetics and storage capacity. For MM-1 material, we found an absorption temperature of about 240 °C is the most optimum. With a maximum hydrogen supply pressure at 120-150 PSI, more than 90% of the hydrogen was absorbed within two hours. With higher hydrogen delivery pressure, the absorption process time will be further reduced. Figure 5 plots the percent of hydrogen desorbed versus time (i.e. desorption rate) of MM-1 at 240 °C. At this temperature, 90% of the hydrogen was released within one hour.

### Example 2

Another MM-1 material was produced by the process described in Example 1 with a change in sintering/annealing temperature. Figure 6 plots the PCT curves of samples sintered/annealed at 570 °C and 600 °C respectively. While the PCT of the material sintered/annealed at 570 °C shows little deviation from that of the material of Example 1 (which was sintered/annealed at 500 °C), the material sintered/annealed at 600 °C provides an extended plateau at a slightly higher pressure.

### Example 3

The mechanically alloyed (MA) powders of MM-1 were prepared from mixtures of pure elemental magnesium (99.8%, -325 mesh), aluminum (99.5%, -325 mesh), and iron (99.9+%, 10 micron). The milling was carried out in an attritor loaded with Cr-steel grinding balls. The

mechanical alloying process is performed under an argon atmosphere with the addition of 1% graphite and heptane to keep material from caking on the attritor walls. Typical milling time is two hours. Figure 7 is an SEM back-scattering micrograph of this sample. The figure indicates severe phase segregation within the material. Region 1 (bright contrast on the picture) is filled with Fe and Al powder while Region 2 (central darker area) is all magnesium. Figure 8, which is the XRD plot of the sample, shows no indication of any amorphous intermetallic product formed by this process. The MA-MM-1 powder was pressed onto an expanded nickel metal substrate and then coated on both sides with 100 angstroms of iron as surface catalysis.

Figure 9 is a plot of the PCT curve measured at 240 °C for the MA-MM-1. The pressure plateau is higher than that of the sintered MM-1 due to the varied distance between Mg-storage phase and Fe-catalytic phase and shows a spectrum of varying kinetics. The maximum hydrogen storage capacity was increased from 5.0 to 5.7% and the hydrogen is fully desorbed at 240 °C. Figure 10 plots the PCT absorption curves of the MA-MM-1 sample at 240 °C, 210 °C, 180 °C, and 150 °C. The plateau pressure increases with the temperature. This phenomenon is to be expected from thermo-equilibrium considerations. However, the maximum storage capacity decreases with decreasing in temperature. This characteristic does not fit into the thermo-equilibrium model. We believe this abnormality is due to the influence of temperature on the absorption kinetics. That is, the PCT analysis was done within specific time constraints and thus may underestimate the full hydrogen storage capacity at lower temperature. Higher maximum capacities than measured at these lower temperature may have been achieved if more time was available to achieve equilibrium.

#### Example 4

Raw material with the designed composition of MM-1 was put in an air-operated induction furnace with additional flux to isolate surface from the atmosphere and prevent excessive magnesium evaporation from the metal liquid. Extra argon gas was supplied to the crucible as an isolation



blanket to prevent oxidation of the molten metal. After melting all ingredients in the crucible, the melt was tilted pour into a mold and slowly cooled to room temperature. The composition of the resulting ingot was examined by induction coupled plasma (ICP) analysis and no trace of iron was detected. From this comparative example, it can be seen that conventional induction melting techniques cannot incorporate iron in the Mg bulk.

The Mg-Al Ingot from above was placed in a bottom-poured melt-spinning machine. After raising temperature above the melting point, the liquid was injected onto a water-cooled copper wheel and turned into long ribbon. Figure 11 is an SEM backscattered photomicrograph of the ribbon cross-section which shows a very uniform Mg-Al alloy. The ribbon was then chopped into small pieces and was placed into attritor for the same MA process as described in Example 3. The ground powder was then pressed onto a Ni expanded metal substrate and coated on both faces with 100 angstroms of Fe.

The MS+MA-MM-1 shows very good hydrogen desorption kinetics at relatively low temperatures. Figure 12 shows a PCT plot of this sample measured at 150 °C. The absorption/desorption pressure hysteresis observed is due to the low measuring temperature. Nevertheless, a desorption plateau at 250 torr is very exciting. Figure 13 compares the maximum reversible hydrogen storage capacities at various temperatures for the three different processes (i.e. sintering, MA-only, MS + MA). The MS + MA process gives the lowest desorption onset temperature (90° C) but also the lowest maximum reversible capacity due to the non-uniform distribution of the Fe phase. The MA-only sample shows the highest desorption temperature onset (150° C) but with the highest reversible storage capacity.

#### Example 5

Raw materials with the nominal composition of MM-1 were put in an air-operated induction furnace with additional flux to isolate the molten surface from the atmosphere and prevent excessive

magnesium evaporation from the liquid metal. Extra argon gas was supplied to the crucible as an isolation blanket to prevent oxidation of the metal. The molten alloy was stirred manually to uniformly suspend immiscible FeAl and Fe phases in the liquid. The liquid was tilt-poured through an argon protected ladle into a water-cooled quenching mold to incorporate the Fe and FeAl phases into the final product. Figure 14 is an SEM micrograph of a cross-section of the resulting ingot which reveals a uniform distribution of FeAl and Fe secondary phase in the Mg host matrix. The Fe-inclusion is about 1 micron in size. The ICP analysis conformed the existence of Fe and Al in the ingot. Other bulk quick quenching methods such as melt spinning, centrifugal atomization, gas atomization, water atomization, with proper stirring in the liquid, such as secondary stirring coil, inert gas bubbling, rotating crucible, etc. may reach similar results. Figure 15 is a schematic depiction of the microstructure of the hydrogen storage powder materials produced by various processing methods of the instant invention. All methods are capable of making reversible hydrogen storage at a substantially lower temperature than the prior art.

The drawings, discussion, descriptions, and examples of this specification are merely illustrative of particular embodiments of the invention and are not meant as limitations upon its practice. It is the following claims, including all equivalents, that define the scope of the invention.